

# Dynamics of heat transfer between nano systems

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We develop a dynamical theory of heat transfer between two nano systems. In particular, we consider the resonant heat transfer between two nanoparticles due to the coupling of localized surface modes having a finite spectral width. We model the coupled nanosystem by two coupled quantum mechanical oscillators, each interacting with its own heat bath, and obtain a master equation for the dynamics of heat transfer. The damping rates in the master equation are related to the lifetimes of localized plasmons in the nanoparticles. We study the dynamics towards the steady state and establish connection with the standard theory of heat transfer in steady state. For strongly coupled nano particles we predict Rabi oscillations in the mean occupation number of surface plasmons in each nano particle.

## I. INTRODUCTION

The theory of heat transfer between nanosystems has been developed for a steady state which is usually characterized by time scales much larger than the relaxation time scale of surface plasmon excitations. However, such time scales are nowadays accessible experimentally [1]. In particular, in the case of long range plasmons [2] these relaxation times could be quite long, demanding the study of the dynamics of heat transfer.

In addition, nearly all the works studying radiative heat transfer at the nanoscale rely on Rytov's fluctuational electrodynamics [3] which is based on the fluctuation-dissipation theorem of the second kind [4, 5], and on macroscopic Maxwell equations. This theoretical framework was very successful in the past. Indeed, the seminal works by Lifshitz, and by Polder and van Hove [6, 7], paved the way for numerous studies of Casimir-Lifshitz forces and nanoscale radiative heat transfer. As a matter of fact, the main assumption in Rytov's theory is that the considered systems are in local thermal equilibrium. By introducing macroscopic thermal fluctuating currents or dipole moments it is therefore possible to relate the correlation functions of the currents or dipoles to the material properties by applying the fluctuation-dissipation theorem. Therefore, the theory is a phenomenological one which has no microscopic justification and enables one to study stationary or quasi-stationary situations only [8]. A genuinely microscopic quantum mechanical description for the heat transfer problem was provided by Janowicz *et al.* [9] using the Caldera-Legget model. But again, this work restricts itself to the steady state, showing that this quantum mechanical description leads to the same results for the heat transfer problem as Rytov's theory.

In this work, we will introduce a simple quantum mechanical model which allows us to study the dynamics of the heat transfer rate between two nanosystems in general and between two nanoparticles in particular. To keep our model simple we will right from the start assume that we have only two nanoparticles supporting localized surface modes which are assumed to provide the main heat flux channel [10]. By this assumption we neglect any contribution due to eddy currents [11, 12], crossed electromagnetic interaction [13], multipoles [14], non-Debye relaxation inside the nanoparticle [15], and many-particle effects [16]. Then, the nanoparticles can be modeled as quantum mechanical oscillators which are coupled due to the interaction of the localized surface modes through their electromagnetic fields. Since we are interested in the heat flow, both nanoparticles are coupled to their own

heat baths. By deriving the master equation for this system we can determine the dynamics of the heat transfer rate towards the steady state. We establish the connection of our model to the results obtained from Rytov's theory [11, 17, 18] by comparison with the steady state solutions of our model.

The structure of the paper is as follows: In section II we motivate and introduce our model. The master equation is derived in section III, where we also determine the analytical solutions as well as the short- and large-time limits of these solutions and the lowest order perturbation results. In section IV we define the heat transfer rate and show how it can be derived using Fermi's golden rule. Finally, in section V we compare the steady-state result of our model with the known steady-state solutions for the heat transfer rate between two nanoparticles determining the coupling constant parameter of our model. In this section we also discuss the relaxation dynamics of the heat transfer rate between two nanoparticles.

## II. PHYSICAL MODEL FOR THE DYNAMICS OF HEAT TRANSFER BETWEEN NANO SYSTEMS

The aim of our work is to study the heat transfer dynamics between two nanosystems. In particular, we model the resonant heat transfer between two nanoparticles which support localized surface modes by means of a quantum mechanical approach. Our model is motivated by the fact that nanoparticles or nanosystems which have an extension smaller than the wavelength of the impinging electromagnetic field can be described by a dipole moment  $\mathbf{p}$  which is induced by the field. This induced dipole moment is related to the incoming field  $\mathbf{E}$  by [19]

$$\mathbf{p} = \epsilon_0 \alpha(\omega) \mathbf{E} \quad (1)$$

where  $\alpha$  is the polarizability of the nanoparticle and  $\epsilon_0$  is the permittivity of vacuum. The resonance of the nanoparticle is determined by the poles of the polarizability. For metallic nanoparticles this resonance can be attributed to collective charge density oscillations within the particle which are called localized surface plasmons.

Considering a very small spherical nanoparticle the polarizability can be expressed as [19]

$$\alpha(\omega) = 4\pi r_0^3 \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}, \quad (2)$$

where  $r_0$  is the radius of the nanoparticle and  $\epsilon$  is its permittivity. From this expression

for the polarizability it becomes apparent that the resonance of the nanoparticle is given by  $\epsilon(\omega) = -2$ . This implicit equation can in general be solved for a complex frequency  $\omega = \omega_{\text{sp}} - i\Gamma$  which determines the oscillation frequency  $\omega_{\text{sp}}$  of the localized charge oscillation and its damping or spectral width  $\Gamma$  due to losses inside the nanoparticle. For Drude metals with the permittivity

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_{\text{p}}^2}{\omega(\omega + i\gamma)} \quad (3)$$

where  $\omega_{\text{p}}$  is the plasma frequency,  $\epsilon_{\infty}$  the background permittivity and  $\gamma$  a phenomenological damping constant we find  $\omega_{\text{sp}} = \omega_{\text{p}}/\sqrt{\epsilon_{\infty} + 2}$  and  $\Gamma = \gamma/2$  for  $\omega_{\text{p}} \gg \gamma$  which is in general the case.

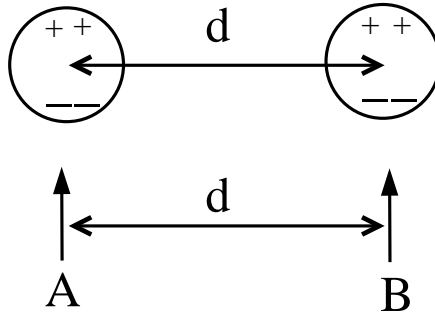


Figure 1: Sketch of the situation considered. Two nanoparticles separated by a distance  $d$  are effectively replaced by two dipoles oscillating with the surface mode resonance frequency  $\omega_{\text{sp}}$ .

Let us now assume that we have two identical nanoparticles  $A$  and  $B$  as sketched in Fig. 1. Particle  $A$  has some nonzero temperature  $T_1$  and particle  $B$  has temperature  $T_2 = 0$ . Then localized surface modes will be excited inside particle  $A$  due to the thermal fluctuations of the charges inside that particle if  $K_{\text{B}}T_1 \approx \hbar\omega_{\text{sp}}$ , where  $K_{\text{B}}$  is Boltzmann's constant and  $\hbar$  is Planck's constant. The thermally excited resonant charge oscillations generate a dipole field which will excite localized charge oscillations inside particle  $B$ . Since the charge oscillations are damped inside particle  $B$  a part of the excitation energy will be converted into heat and particle  $B$  heats up, whereas particle  $A$  cools down. Of course, the charge oscillations inside particle  $B$  will also excite charge oscillations in particle  $A$  and so forth. So that we can expect that energy will be transferred back and forth between the particles until a steady state or equilibrium situation is reached.

The heat flux between two nanoparticles within the steady state can be calculated by using the fluctuation-dissipation theorem [4, 5] and was for example studied in Ref. [11].

Here, we are interested in the dynamics of the relaxation towards the steady state which amounts to apply a full non-equilibrium description. To this end, we first chose to describe the two nanoparticles as quantum mechanical oscillators  $A$  and  $B$  having a frequency  $\omega_{\text{sp}}$ . The Hamiltonian of the two oscillators is

$$H_0 = \hbar\omega_{\text{sp}}a^\dagger a + \hbar\omega_{\text{sp}}b^\dagger b. \quad (4)$$

Here  $a^\dagger$ ,  $a$  and  $b^\dagger$ ,  $b$  are the creation and annihilation operators associated to oscillator  $A$  and  $B$  which fulfill the bosonic commutation relations  $[a, a^\dagger] = [b, b^\dagger] = 1$ . Note, that the zero point contribution is not taken into account, since it does not affect the dynamics.

The interaction of the two nanoparticles which is attributed to the coupled charge oscillations is now taken into account by a linear coupling between oscillator  $A$  and  $B$  of the form

$$H_1 = \hbar g(b^\dagger a + a^\dagger b). \quad (5)$$

That means we allow for the exchange of photons (single photon process) between the two oscillators. The first term describes the photon transfer from particle  $A$  to particle  $B$ , i.e.  $|n_A, n_B\rangle \rightarrow |n_A - 1, n_B + 1\rangle$ , whereas the second term describes the photon transfer from particle  $B$  to particle  $A$ , i.e.  $|n_A, n_B\rangle \rightarrow |n_A + 1, n_B - 1\rangle$ . The quantity  $g$  can be estimated by a variety of methods — one of which is described in Sec V. The most direct and general method is to use an analog of the mode-mode coupling theory as in case of waveguides [20]. The parameter  $g$  is essentially given by the overlap of the plasmon field produced by the nanoparticle  $A$  with the plasmon field of the nano particle  $B$ . Note that if  $g \ll \Gamma$  then we are in the perturbative regime, however for  $g \gg \Gamma$  we have non-perturbative regime where Rabi oscillations occur. The situation is somewhat reminiscent of cavity QED [21].

Since both nanoparticles can attain a temperature we couple each oscillator to its own heat bath which consist of a spectrum of independent oscillators [25] described by the two Hamiltonians

$$H_{B1} = \sum_j \hbar\omega_{1j}a_{1j}^\dagger a_{1j}, \quad (6)$$

$$H_{B2} = \sum_j \hbar\omega_{2j}a_{2j}^\dagger a_{2j}. \quad (7)$$

Again the creation and annihilation operators  $a_{1j}^\dagger$ ,  $a_{1j}$  and  $a_{2j}^\dagger$ ,  $a_{2j}$  fulfill the bosonic commutation relations  $[a_{1i}, a_{1j}^\dagger] = [a_{2i}, a_{2j}^\dagger] = \delta_{ij}$ ;  $\omega_{1j}$  and  $\omega_{2j}$  are the oscillator frequencies. We

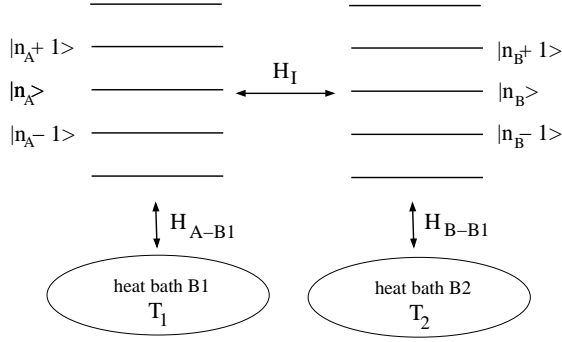


Figure 2: Sketch of our model consisting of two harmonic oscillator  $A$  and  $B$  interacting through  $H_I$ . Each oscillator is coupled to a heat bath of independent oscillators in equilibrium at temperatures  $T_1$  and  $T_2$ .

assume that both heat baths are in thermal equilibrium at temperatures  $T_1$  and  $T_2$ , i.e. the density operators of the heat baths are given by

$$\rho_{B1/B2} = \frac{e^{-\beta_{1/2} H_{B1/B2}}}{\text{Tr}(e^{-\beta_{1/2} H_{B1/B2}})} \quad (8)$$

where  $\beta_{1/2} = 1/K_B T_{1/2}$  is the inverse temperature.

We further assume that each nanoparticle described by the harmonic oscillators  $A$  and  $B$  is linearly coupled to its heat bath  $B1$  and  $B2$ . The corresponding Hamiltonians are given by

$$H_{A-B1} = \hbar i \sum_j g_{1j} (a + a^\dagger)(a_{1j} - a_{1j}^\dagger), \quad (9)$$

$$H_{B-B2} = \hbar i \sum_j g_{2j} (b + b^\dagger)(a_{2j} - a_{2j}^\dagger) \quad (10)$$

introducing the coupling strengths  $g_{1j}$  and  $g_{2j}$  which are related to the damping  $\Gamma$  of the charge oscillations modeled by the oscillators  $A$  and  $B$ . When assuming that both reservoirs are in thermal equilibrium at temperatures  $T_1$  and  $T_2$  and there is no interaction between oscillator  $A$  and  $B$  ( $g = 0$ ), then by means of this coupling to their heat baths both oscillators will in the long-time limit reach an equilibrium state described by the reduced density operators

$$\rho_{A/B} = \frac{e^{-\beta_{1/2} H_{A/B}}}{\text{Tr}(e^{-\beta_{1/2} H_{A/B}})} \quad (11)$$

where  $H_A = \hbar\omega_{\text{sp}} a^\dagger a$  and  $H_B = \hbar\omega_{\text{sp}} b^\dagger b$ . Hence, the two harmonic oscillators  $A$  and  $B$  would acquire the temperatures of their heat baths if there is no coupling, i.e.  $g = 0$ . Since in our

model the coupling  $g \neq 0$  between the oscillators  $A$  and  $B$  they will in general not acquire the temperatures of their reservoirs in the long-time limit.

Putting all the different terms together the Hamiltonian of our model sketched in Fig. 2 is given by

$$H = H_0 + H_I + H_{B1} + H_{B2} + H_{A-B1} + H_{B-B2}. \quad (12)$$

For later reference we introduce  $H_S = H_0 + H_I$  which is the Hamiltonian of a system of two coupled harmonic oscillors without any reservoir.

### III. MASTER EQUATION

In order to determine the dynamics of the system of two coupled harmonic oscillators we first derive the master equation of the reduced coupled-oscillator system  $H_S$ . Using the standard Born-Markov approximation in combination with the rotating wave approximation [25] and tracing out the bath variables using the density operators  $\rho_{B1}$  and  $\rho_{B2}$  from Eq. (8) we obtain the master equation

$$\begin{aligned} \frac{\partial \rho_S}{\partial t} = & -i\omega_a[a^\dagger a, \rho_S] - i\omega_b[b^\dagger b, \rho_S] \\ & - ig[a^\dagger b + b^\dagger a, \rho_S] \\ & - \kappa_1(\bar{n}_1 + 1)(a^\dagger a \rho_S - 2a \rho_S a^\dagger + \rho_S a^\dagger a) \\ & - \kappa_1 \bar{n}_1(a a^\dagger \rho_S - 2a^\dagger \rho_S a + \rho_S a a^\dagger) \\ & - \kappa_2(\bar{n}_2 + 1)(b^\dagger b \rho_S - 2b \rho_S b^\dagger + \rho_S b^\dagger b) \\ & - \kappa_2 \bar{n}_2(b b^\dagger \rho_S - 2b^\dagger \rho_S b + \rho_S b b^\dagger) \end{aligned} \quad (13)$$

where the coupling constants

$$\kappa_1 = \pi \sum_j g_{1j}^2 \delta(\omega_{1j} - \omega_a), \quad (14)$$

$$\kappa_2 = \pi \sum_j g_{2j}^2 \delta(\omega_{2j} - \omega_b) \quad (15)$$

can in our model be identified as the linewidths  $\Gamma$  of the localized surface modes. We have also introduced the mean occupation numbers

$$\bar{n}_{1/2} = \frac{1}{e^{\hbar\beta_{1/2}\omega_{a/b}} - 1} \quad (16)$$

stemming from the trace over the bath oscillators which are assumed to be in thermal equilibrium at temperatures  $T_1$  and  $T_2$ . For the sake of generality and later use we have here assumed that the frequencies  $\omega_a$  and  $\omega_b$  of the oscillators  $A$  and  $B$  are different. In a later stage, we will set these frequencies to  $\omega_a = \omega_b = \omega_{\text{sp}}$ .

The master equation allows us now to determine the dynamical equations of the mean values  $\langle a^\dagger a \rangle$ ,  $\langle b^\dagger b \rangle$ ,  $\langle a^\dagger b \rangle$  and  $\langle b^\dagger a \rangle$ . By using the commutation relations of the creation and annihilation operators for both oscillators we obtain the set of equations

$$\frac{d}{dt}\langle a^\dagger a \rangle = -ig(\langle a^\dagger b \rangle - \langle b^\dagger a \rangle) - 2\kappa_1\langle a^\dagger a \rangle + 2\kappa_1\bar{n}_1, \quad (17)$$

$$\frac{d}{dt}\langle b^\dagger b \rangle = -ig(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) - 2\kappa_2\langle b^\dagger b \rangle + 2\kappa_2\bar{n}_2, \quad (18)$$

$$\frac{d}{dt}\langle b^\dagger a \rangle = \Omega_{ab}\langle b^\dagger a \rangle - ig(\langle b^\dagger b \rangle - \langle a^\dagger a \rangle), \quad (19)$$

$$\frac{d}{dt}\langle a^\dagger b \rangle = \Omega_{ba}\langle a^\dagger b \rangle - ig(\langle a^\dagger a \rangle - \langle b^\dagger b \rangle), \quad (20)$$

where for the sake of clarity we have introduced the new quantities

$$\Omega_{ab} = -i(\omega_a - \omega_b) - \kappa_1 - \kappa_2, \quad (21)$$

$$\Omega_{ba} = +i(\omega_a - \omega_b) - \kappa_1 - \kappa_2. \quad (22)$$

### A. Steady state solutions

The steady state solutions of the dynamical equations can now be obtained by setting all time derivatives  $\frac{d}{dt}\langle a^\dagger a \rangle$ ,  $\frac{d}{dt}\langle b^\dagger b \rangle$  etc. equal to zero. Solving the resulting set of equations we obtain

$$\langle a^\dagger a \rangle = \frac{A(\kappa_1\bar{n}_1 + \kappa_2\bar{n}_2) + 2\kappa_1\kappa_2\bar{n}_1}{A(\kappa_1 + \kappa_2) + 2\kappa_1\kappa_2}, \quad (23)$$

$$\langle b^\dagger b \rangle = \frac{A(\kappa_1\bar{n}_1 + \kappa_2\bar{n}_2) + 2\kappa_1\kappa_2\bar{n}_2}{A(\kappa_1 + \kappa_2) + 2\kappa_1\kappa_2}, \quad (24)$$

$$\langle b^\dagger a \rangle = \frac{ig}{\Omega_{ab}} \frac{2\kappa_1\kappa_2(\bar{n}_2 - \bar{n}_1)}{(\kappa_1 + \kappa_2)A + 2\kappa_1\kappa_2}, \quad (25)$$

$$\langle a^\dagger b \rangle = -\frac{\Omega_{ab}}{\Omega_{ba}}\langle b^\dagger a \rangle, \quad (26)$$

with

$$A = -g^2 \frac{\Omega_{ab} + \Omega_{ba}}{\Omega_{ab}\Omega_{ba}} = g^2 \frac{2(\kappa_1 + \kappa_2)}{(\kappa_1 + \kappa_2)^2 + (\omega_a - \omega_b)^2}. \quad (27)$$



The steady state expressions allow us to check the plausibility of our approach. If we set for example the coupling between the two oscillators to zero ( $g = 0$ ), then we find  $\langle a^\dagger a \rangle = \bar{n}_1$  and  $\langle b^\dagger b \rangle = \bar{n}_2$ . That means that the two uncoupled oscillators acquire the temperatures of their heat baths, as expected. If we cut off one of the heat baths by setting  $\kappa_1 = 0$  ( $\kappa_2 = 0$ ), then we find  $\langle a^\dagger a \rangle = \langle b^\dagger b \rangle = \bar{n}_2$  ( $\langle a^\dagger a \rangle = \langle b^\dagger b \rangle = \bar{n}_1$ ) which means that in this case both oscillators take the temperature of the remaining heat bath. Finally, if we let the coupling between the two oscillators go to infinity ( $l \rightarrow \infty$ ) then we find

$$\langle a^\dagger a \rangle = \langle b^\dagger b \rangle = \frac{\kappa_1}{\kappa_1 + \kappa_2} \bar{n}_1 + \frac{\kappa_2}{\kappa_1 + \kappa_2} \bar{n}_2. \quad (28)$$

In this case, both oscillators are not in an equilibrium state with one of the reservoirs anymore. Their mean occupation number is the sum of the equilibrium occupation numbers of both reservoirs weighted by the relative coupling strength.

## B. Full dynamical solutions

We will now derive the full dynamical solutions by setting  $\omega_a = \omega_b = \omega_{\text{sp}}$ . This corresponds to the situation of a resonant coupling in which we are interested and it simplifies our problem, since then  $\Omega_{ab} = \Omega_{ba} = -(\kappa_1 + \kappa_2)$ . It follows that the set of four coupled differential equations can be recasted into a set of only 3 coupled differential equations by subtracting the last two differential equations (19) and (20) from each other and by considering  $\langle b^\dagger a \rangle - \langle a^\dagger b \rangle$  as a new dynamical variable. Furthermore we assume that the second heat bath has zero temperature, i.e. we set  $\bar{n}_2 = 0$ . Then the 3 coupled differential equations can be stated as

$$\dot{\mathbf{x}} = \mathbb{A} \mathbf{x} + \mathbf{a} \quad (29)$$

with  $\mathbf{x} = (\langle a^\dagger a \rangle, \langle b^\dagger b \rangle, \langle b^\dagger a \rangle - \langle a^\dagger b \rangle)^t$ ,  $\mathbf{a} = (2\kappa_1 \bar{n}_1, 0, 0)$ , and

$$\mathbb{A} = \begin{pmatrix} -2\kappa_1 & 0 & g \\ 0 & -2\kappa_2 & -g \\ 2g & -2g & -(\kappa_1 + \kappa_2) \end{pmatrix}. \quad (30)$$

This set of coupled first order differential equations can be solved by hand in a standard fashion. First we determine the eigenvalues of  $\mathbb{A}$  by solving the characteristic equation

$\det(\mathbb{A} - \lambda \mathbb{1}) = 0$ . We obtain the three eigenvalues

$$\lambda_1 = -(\kappa_1 + \kappa_2), \quad (31)$$

$$\lambda_{2,3} = -(\kappa_1 + \kappa_2) \pm \sqrt{(\kappa_1 - \kappa_2)^2 + 4g^2}. \quad (32)$$

Then we diagonalize matrix  $\mathbf{A}$  by introducing the matrix  $\mathbb{S}$  consisting of the eigenvectors of  $\mathbb{A}$  such that

$$\mathbb{S}^{-1} \mathbb{A} \mathbb{S} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \equiv \mathbb{B}. \quad (33)$$

By means of the matrices  $\mathbb{S}$  and  $\mathbb{S}^{-1}$  we decouple the set of coupled differential equations which translate into

$$\dot{\mathbf{y}} = \mathbb{B} \mathbf{y} + \mathbf{b}. \quad (34)$$

Here  $\mathbf{y} = \mathbb{S}^{-1} \mathbf{x}$  and  $\mathbf{b} = \mathbb{S}^{-1} \mathbf{a}$ . Since  $\mathbf{a} = (2\kappa_1 \bar{n}_1, 0, 0)^t$ ,  $\mathbf{b}$  equals the first column of  $\mathbb{S}^{-1}$  times  $2\kappa_1 \bar{n}_1$ . We have now three decoupled inhomogeneous differential equations ( $i = 1, 2, 3$ )

$$\dot{y}_i = \lambda_i y_i + b_i. \quad (35)$$

which have the solution

$$y_i = e^{\lambda_i t} \eta_i + (e^{\lambda_i t} - 1) \frac{b_i}{\lambda_i} \quad (36)$$

where the first term represents the homogeneous solution with a prefactor  $\eta_i$  which is determined by the initial conditions at  $t = 0$ . The second term represents the inhomogeneous solution which vanishes for  $t = 0$ .

From these solutions of the decoupled problem, one can calculate the corresponding solutions of the coupled set of differential equations by  $\mathbf{x} = \mathbb{S} \cdot \mathbf{y}$ . Finally, imposing the initial conditions

$$\left. \langle a^\dagger a \rangle \right|_{t=0} = \bar{n}_1, \quad \left. \langle b^\dagger b \rangle \right|_{t=0} = 0, \quad \text{and} \quad \left. (\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) \right|_{t=0} = 0 \quad (37)$$

which means that at  $t = 0$  oscillator  $A$  has the temperature of its heat bath, oscillator  $B$  has zero temperature (which is the temperature of the second heat bath), and that at  $t = 0$  the photon transfer is just turned on, one can determine  $\eta_i$ . The solution for  $\mathbf{x}$  fulfilling these

initial conditions can be written as

$$\mathbf{x} = \begin{pmatrix} \sum_i x_i \eta_i \left( e^{\lambda_i t} + \frac{2\kappa_1}{\lambda_i} [e^{\lambda_i t} - 1] \right) \\ \sum_i y_i \eta_i \left( e^{\lambda_i t} + \frac{2\kappa_1}{\lambda_i} [e^{\lambda_i t} - 1] \right) \\ \sum_i \eta_i \left( e^{\lambda_i t} + \frac{2\kappa_1}{\lambda_i} [e^{\lambda_i t} - 1] \right) \end{pmatrix} \quad (38)$$

where

$$x_i = \frac{g}{2\kappa_1 + \lambda_i} \quad \text{and} \quad y_i = -\frac{g}{2\kappa_2 + \lambda_i}, \quad (39)$$

and

$$\eta_1 = \bar{n}_1 \frac{y_3 - y_2}{N}, \quad (40)$$

$$\eta_2 = \bar{n}_1 \frac{y_1 - y_3}{N}, \quad (41)$$

$$\eta_3 = \bar{n}_1 \frac{y_2 - y_1}{N}, \quad (42)$$

$$N = (x_2 - x_1)(y_1 - y_3) + (x_3 - x_1)(y_2 - y_1). \quad (43)$$

In Figs. 3 we show some plots of the analytical expressions for  $\langle a^\dagger a \rangle / \bar{n}_1$ ,  $\langle b^\dagger b \rangle / \bar{n}_1$ ,  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$  and over time choosing  $\kappa_1 = \kappa_2 \equiv \kappa$  and different coupling strengths  $g/\kappa$  between oscillator  $A$  and oscillator  $B$ . First of all, we can see that the mean occupation number  $\langle a^\dagger a \rangle$  of oscillator  $A$  reaches in the long-time limit a constant value smaller than its initial value  $\bar{n}_1$ , whereas the mean occupation number  $\langle b^\dagger b \rangle$  of oscillator  $B$  converges in the long-time limit to a constant value larger than its initial value 0. Therefore, we observe an energy transfer from oscillator  $A$  to oscillator  $B$ . This energy transfer is related  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$  as we will see later. For small coupling strengths the evolution of the occupation numbers is monotonic, but for large coupling strengths one can observe an oscillatory behavior. Hence, the energy is going back and forth between both oscillators until the steady state is reached. This behaviour is analogous to the Rabi oscillations observed for a two-level system coupled to a field including radiative damping, two coupled qubits, or coupled exciton-plasmon systems for instance [1, 22–24]. In such systems Rabi oscillations are found in the strong-coupling limit which corresponds in our case to  $g/\kappa \gg 1$ , whereas in the weak-coupling limit (here  $g/\kappa \ll 1$ ) these oscillations are damped out [22, 24].

In Fig. 4 we show  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$  over time for  $g/\kappa = 10$  together with  $\langle a^\dagger a \rangle / \bar{n}_1$  and  $\langle b^\dagger b \rangle / \bar{n}_1$ . As we will see later,  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$  is proportional to the energy transfer

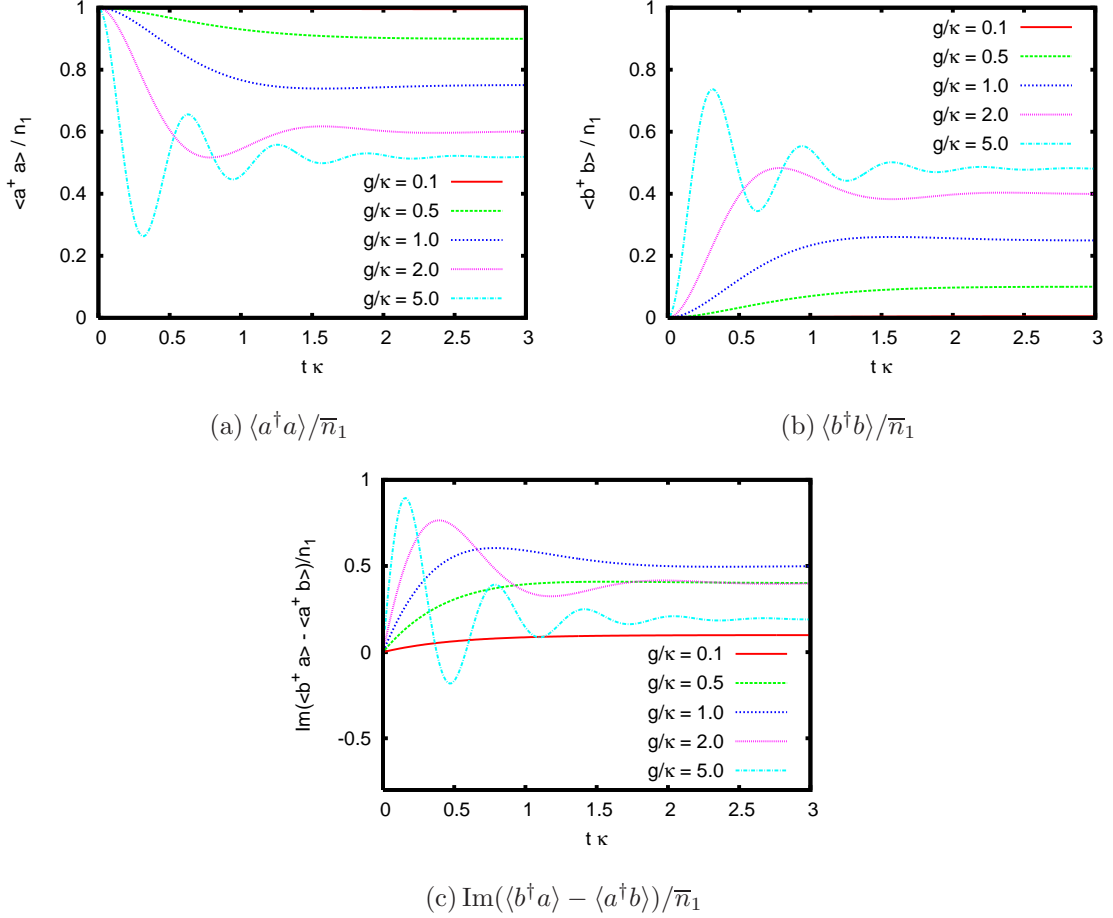


Figure 3: Plot of (a)  $\langle a^\dagger a \rangle / \bar{n}_1$ , (b)  $\langle b^\dagger b \rangle / \bar{n}_1$  and (c)  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$  over time for  $\kappa_1 = \kappa_2 \equiv \kappa$  and different coupling strengths  $g/\kappa$ . For large  $t$  the solutions converges to the steady state solutions found in Eqs. (23) and (24) for  $\Omega_{ab} = \Omega_{ba} = -(\kappa_1 + \kappa_2)$  and  $\bar{n}_2 = 0$ .

between oscillator  $A$  and  $B$ . From Fig. 4 we see that the oscillations of  $\langle b^\dagger b \rangle$  are phase shifted by  $\pi$  with respect to the oscillations of  $\langle a^\dagger a \rangle$  and the oscillations of  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$  have a phase shift of  $\pi/2$  with respect to  $\langle a^\dagger a \rangle$  and  $\langle b^\dagger b \rangle$ .

Since we are interested in the energy transfer from oscillator  $A$  to oscillator  $B$  let us further analyse  $\langle b^\dagger b \rangle$  and  $\langle b^\dagger a \rangle - \langle a^\dagger b \rangle$  and derive the short- and large-time limits. From the

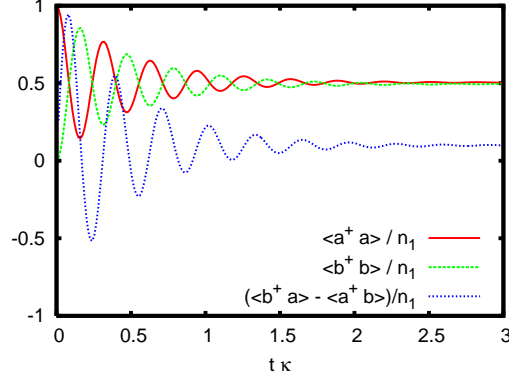


Figure 4: Plot of  $\text{Im}(\langle b^\dagger a \rangle - \langle a^\dagger b \rangle) / \bar{n}_1$ ,  $\langle a^\dagger a \rangle / \bar{n}_1$ , and  $\langle b^\dagger b \rangle / \bar{n}_1$  over time for  $\kappa_1 = \kappa_2 = 1 \equiv \kappa$  and  $g/\kappa = 10$ .

analytical solutions we find

$$\langle b^\dagger b \rangle \approx \begin{cases} \bar{n}_1 g^2 t^2 & t \ll \kappa_1^{-1}, \kappa_2^{-1} \\ \frac{g^2 \bar{n}_1}{\kappa_2(\kappa_1 + \kappa_2)} \frac{1}{1 + \frac{g^2}{\kappa_1 \kappa_2}} & t \gg \kappa_1^{-1}, \kappa_2^{-1} \end{cases} \quad (44)$$

$$\langle b^\dagger a \rangle - \langle a^\dagger b \rangle \approx \begin{cases} 2\bar{n}_1 i g t & t \ll \kappa_1^{-1}, \kappa_2^{-1} \\ + \frac{2i g \bar{n}_1}{(\kappa_1 + \kappa_2)} \frac{1}{1 + \frac{g^2}{\kappa_1 \kappa_2}} & t \gg \kappa_1^{-1}, \kappa_2^{-1} \end{cases}. \quad (45)$$

We see that  $\langle b^\dagger a \rangle - \langle a^\dagger b \rangle$  is linear in  $gt$  and  $\langle b^\dagger b \rangle$  is quadratic in  $gt$  for times  $t \ll \kappa_1^{-1}, \kappa_2^{-1}$ . For times  $t \gg \kappa_1^{-1}, \kappa_2^{-1}$  we retrieve the steady-state results derived in Eqs. (23) and (24) for the case  $\Omega_{ab} = \Omega_{ba} = -(\kappa_1 + \kappa_2)$  and  $\bar{n}_2 = 0$ . Furthermore, we see that for  $t \gg \kappa_1^{-1}, \kappa_2^{-1}$

$$\langle b^\dagger b \rangle \propto g^2 \left( 1 - \frac{g^2}{\kappa_1 \kappa_2} + \dots \right), \quad (46)$$

$$\langle b^\dagger a \rangle - \langle a^\dagger b \rangle \propto g \left( 1 - \frac{g^2}{\kappa_1 \kappa_2} + \dots \right). \quad (47)$$

From this one can expect that  $\langle b^\dagger b \rangle$  has only even orders in  $g$ , whereas  $\langle b^\dagger a \rangle - \langle a^\dagger b \rangle$  has only odd orders in  $g$ .

### C. Perturbation expansion

To complete the analysis, we also derive the perturbation result of the set of differential equations (17)-(20) for  $\langle b^\dagger b \rangle$  and  $\langle b^\dagger a \rangle - \langle a^\dagger b \rangle$  in orders of  $g$ . Here again we first consider the general case  $\Omega_{ab} \neq \Omega_{ba}$ . Expanding  $\langle a^\dagger a \rangle = \langle a^\dagger a \rangle^{(0)} + \langle a^\dagger a \rangle^{(1)} + \langle a^\dagger a \rangle^{(2)} + \dots$ ,  $\langle b^\dagger b \rangle =$

$\langle b^\dagger b \rangle^{(0)} + \langle b^\dagger b \rangle^{(1)} + \langle b^\dagger b \rangle^{(2)} + \dots$  etc. and solving the dynamical equations for the different perturbation orders. We find for the lowest orders giving nonvanishing contributions

$$\langle b^\dagger a \rangle^{(1)} - \langle a^\dagger b \rangle^{(1)} = ig\bar{n}_1 \left[ \frac{e^{\Omega_{ab}t} - 1}{\Omega_{ab}} + \frac{e^{\Omega_{ba}t} - 1}{\Omega_{ba}} \right] \quad (48)$$

and

$$\langle b^\dagger b \rangle^{(2)} = g^2 \bar{n}_1 \left[ \frac{e^{\Omega_{ab}t} - e^{-2\kappa_2 t}}{\Omega_{ab}(2\kappa_2 + \Omega_{ab})} + \frac{e^{\Omega_{ba}t} - e^{-2\kappa_2 t}}{\Omega_{ba}(2\kappa_2 + \Omega_{ba})} + \frac{e^{-2\kappa_2 t} - 1}{2\kappa_2} \frac{\Omega_{ab} + \Omega_{ba}}{\Omega_{ab}\Omega_{ba}} \right]. \quad (49)$$

As expected  $\langle b^\dagger b \rangle^{(1)} = 0$ .

To compare these results with the analytical solutions we set  $\omega_a = \omega_b = \omega_{\text{sp}}$ , i.e.  $\Omega_{ab} = \Omega_{ba} = -(\kappa_1 + \kappa_2)$ . Then we find the short and long time limits

$$\langle b^\dagger a \rangle^{(1)} - \langle a^\dagger b \rangle^{(1)} \approx \begin{cases} 2\bar{n}_1 i g t & t \ll \kappa_1^{-1}, \kappa_2^{-1} \\ \frac{2ig\bar{n}_1}{(\kappa_1 + \kappa_2)} & t \gg \kappa_1^{-1}, \kappa_2^{-1} \end{cases} \quad (50)$$

and

$$\langle b^\dagger b \rangle^{(2)} \approx \begin{cases} \bar{n}_1 g^2 t^2 & t \ll \kappa_1^{-1}, \kappa_2^{-1} \\ \frac{g^2 \bar{n}_1}{(\kappa_1 + \kappa_2)\kappa_2} & t \gg \kappa_1^{-1}, \kappa_2^{-1} \end{cases}. \quad (51)$$

By comparing these perturbation results with the corresponding analytical expressions in (44) and (45) we can infer that in general the perturbation results are valid for  $g^2 \ll \kappa_1 \kappa_2$ . In particular, we find that for  $t \ll \kappa_1^{-1}, \kappa_2^{-1}$  the perturbation result coincides with the analytical solution.

#### IV. HEAT TRANSFER RATE

Before we apply our model to describe the dynamics of heat transfer between two nanoparticles, we will define the energy transfer rate and discuss under which circumstances it can be derived from Fermi's golden rule.

##### A. Defining the energy transfer rate

For two classical harmonic oscillators  $A$  and  $B$  the transferred energy per unit time from  $A$  to  $B$  can be described by the rate of work done on oscillator  $B$  by oscillator  $A$

$$P = k(x_B - x_A) \cdot \dot{x}_B \quad (52)$$

where  $k$  is the spring constant for the spring between the oscillators and  $x_A$  and  $x_B$  are the displacements of the oscillators from their equilibrium position. The quantum mechanical analog can be derived from that expression by replacing

$$x_A \rightarrow (a^\dagger + a)\sqrt{\frac{\hbar}{2m\omega_{\text{sp}}}}, \quad (53)$$

$$x_B \rightarrow (b^\dagger + b)\sqrt{\frac{\hbar}{2m\omega_{\text{sp}}}}, \quad (54)$$

$$\dot{x}_A = \frac{p_A}{m} \rightarrow i(a^\dagger - a)\sqrt{\frac{\hbar\omega_{\text{sp}}}{2m}}, \quad (55)$$

$$\dot{x}_B = \frac{p_B}{m} \rightarrow i(b^\dagger - b)\sqrt{\frac{\hbar\omega_{\text{sp}}}{2m}}. \quad (56)$$

Keeping only terms for which a photon is interchanged between both oscillators, i.e. which allow for the transition processes  $|\bar{n}_1, \bar{n}_2\rangle \rightarrow |\bar{n}_1 - 1, \bar{n}_2 + 1\rangle$  and  $|\bar{n}_1, \bar{n}_2\rangle \rightarrow |\bar{n}_1 + 1, \bar{n}_2 - 1\rangle$ , we obtain

$$P = ki\frac{\hbar}{2m}(ab^\dagger - ba^\dagger). \quad (57)$$

In order to relate the prefactor to the coupling constant  $g$  or  $l$  used in our model, we start with the classical expression for the potential energy

$$H_I = \frac{k}{2}(x_A - x_B)^2 \quad (58)$$

and replace the displacements by the expressions in Eqs. (53) and (54). Keeping again only terms allowing for photon exchange between the oscillators we find

$$H_I = -k\frac{\hbar}{2m\omega_{\text{sp}}}(a^\dagger b + b^\dagger a). \quad (59)$$

By comparing this result with the interaction Hamiltonian of our model in Eq. (5) we find that  $g = -k/2m\omega_{\text{sp}}$ . Hence for the transferred power

$$P = \hbar\omega_{\text{sp}}(-ig)(ab^\dagger - ba^\dagger). \quad (60)$$

### 1. Full expression

Since we know the analytical solution for  $\langle ab^\dagger \rangle - \langle a^\dagger b \rangle$  we can immediately write down the analytical solution for the mean rate of energy transfer

$$\langle P \rangle = \hbar\omega_{\text{sp}}(-ig)[\langle ab^\dagger \rangle - \langle a^\dagger b \rangle] = \hbar\omega_{\text{sp}}R \quad (61)$$

where the energy transfer rate  $R$  is by means of Eq. (38) given by

$$R = -ig \sum_i \eta_i \left[ e^{\lambda_i t} + \frac{2\kappa_1}{\lambda_i} \left( e^{\lambda_i t} - 1 \right) \right]. \quad (62)$$

From this expression we can derive the short-time and large-time limits

$$R \approx \begin{cases} 2\bar{n}_1 g^2 t & t \ll \kappa_1^{-1}, \kappa_2^{-1} \\ \frac{2g^2 \bar{n}_1}{(\kappa_1 + \kappa_2)} \frac{1}{1 + \frac{g^2}{\kappa_1 \kappa_2}} & t \gg \kappa_1^{-1}, \kappa_2^{-1} \end{cases}. \quad (63)$$

Note that in the short-time limit the rate  $R$  is given by  $\partial \langle b^\dagger b \rangle / \partial t$  taking  $\langle b^\dagger b \rangle$  from Eq. (44). On the other hand, in the long-time limit this observation does not remain true. In the regime of Rabi oscillations ( $g \gg \kappa_{1/2}$ ) the rate of transfer is not a meaningful quantity and we have to work with the integrated power.

In the general case ( $n_1 > 0$  and  $n_2 > 0$ ) the expression for the transferred power in Eq. (52) has to be augmented by a term  $-k(x_A - x_B) \cdot \dot{x}_A$  quantifying the rate of power done on oscillator  $A$  by oscillator  $B$ . The resulting expression for  $P$  and  $R$  due to that term is just the same as in Eq. (62), but with  $n_1$  replaced by  $-n_2$ . Hence, the overall transferred energy has a prefactor  $(n_1 - n_2)$  determining the direction of the energy transfer or heat flux, uniquely. It follows that in steady state the energy is always transferred from the hotter to the colder nanosystem.

## 2. Perturbation result

The corresponding expression for the heat transfer rate for small coupling strength is obtained with the help of Eq. (50), giving

$$R \approx -ig [\langle b^\dagger a \rangle^{(1)} - \langle a^\dagger b \rangle^{(1)}] \approx \begin{cases} 2\bar{n}_1 g^2 t & t \ll \kappa_1^{-1}, \kappa_2^{-1} \\ \frac{2g^2 \bar{n}_1}{(\kappa_1 + \kappa_2)} & t \gg \kappa_1^{-1}, \kappa_2^{-1} \end{cases}. \quad (64)$$

As noted above for times  $t \ll \kappa_1, \kappa_2$  the perturbation result and the analytical result coincide, whereas for times  $t \gg \kappa_1, \kappa_2$  the perturbation result is only valid for  $g^2 \ll \kappa_1 \kappa_2$ .

## B. Fermi's golden rule

Finally, we derive the heat transfer rate by using Fermi's golden rule

$$R_{\text{FGR}} = \frac{2\pi}{\hbar^2} |\langle f | H_I | i \rangle|^2 \delta(\omega_f - \omega_i). \quad (65)$$



In our case the initial state is given by a)  $|i\rangle = |n_1, n_2\rangle$  and  $|f\rangle = |n_1 - 1, n_2 + 1\rangle$  describing the photon transfer from oscillator  $A$  to  $B$  and b)  $|i\rangle = |n_1, n_2\rangle$  and  $|f\rangle = |n_1 + 1, n_2 - 1\rangle$  describing the photon transfer from oscillator  $B$  to  $A$ . Inserting the interaction Hamiltonian  $H_I$  from Eq. (5) and taking the difference of process a) and b) we find

$$\begin{aligned} R_{\text{FGR}} &= 2\pi g^2 [n_1(n_2 + 1) - n_2(n_1 + 1)] \delta(\omega_f - \omega_i) \\ &= 2\pi g^2 [n_1 - n_2] \delta(\omega_f - \omega_i). \end{aligned} \quad (66)$$

For the special case that  $n_1 = \bar{n}_1$ ,  $n_2 = \bar{n}_2 = 0$ ,  $\omega_f = \omega_b$ , and  $\omega_i = \omega_a$  we obtain

$$R_{\text{FGR}} = 2\pi g^2 \bar{n}_1 \delta(\omega_a - \omega_b). \quad (67)$$

Now, let us take into account that the oscillators  $A$  and  $B$  have a finite linewidth  $\kappa_1$  and  $\kappa_2$  through their coupling to the reservoirs. Assuming a Lorentzian profile for the linewidth and averaging over these profiles, we obtain (setting  $\omega_a = \omega_b = \omega_{\text{sp}}$ )

$$\begin{aligned} R_{\text{FGR}} &= g^2 \bar{n}_1 2\pi \int d\omega_1 \int d\omega_2 \frac{\kappa_1/\pi}{(\omega_{\text{sp}} - \omega_1)^2 + \kappa_1^2} \frac{\kappa_2/\pi}{(\omega_{\text{sp}} - \omega_2)^2 + \kappa_2^2} \delta(\omega_1 - \omega_2) \\ &= \frac{2g^2 \bar{n}_1}{\kappa_1 + \kappa_2}. \end{aligned} \quad (68)$$

Comparing this expression with the perturbation result for the heat transfer rate in Eq. (64) we see that it is valid for  $t \gg \kappa_1, \kappa_2$  and  $g^2 \ll \kappa_1 \kappa_2$ .

To have a better understanding of the Fermi golden rule expression for the heat transfer rate, let us see how the golden rule is derived from  $\langle b^\dagger b \rangle$ . First, the golden rule is based on time-dependent first order perturbation theory in the transition amplitudes. Therefore, for  $\langle b^\dagger b \rangle$  we have to make a second-order perturbation expansion with respect to the coupling strength. The resulting expression for  $\langle b^\dagger b \rangle$  is already given in Eq. (49). If we cut off the heat baths by setting  $\kappa_1 = \kappa_2 = 0$ , then we arrive at

$$\langle b^\dagger b \rangle^{(2)} = g^2 \bar{n}_1 \frac{\sin^2\left(\frac{\Delta t}{2}\right)}{\left(\frac{\Delta}{2}\right)^2}, \quad (69)$$

where  $\Delta = \omega_a - \omega_b$ . From such expression Fermi's golden rule is usually derived by considering the long-time limit [22]

$$R_{\text{FGR}} = \lim_{t \rightarrow \infty} \frac{\langle b^\dagger b \rangle}{t} = g^2 \bar{n}_1 2\pi \delta(\Delta) \quad (70)$$

which is Fermi's golden rule; we have used that

$$\lim_{t \rightarrow \infty} \frac{\sin^2\left(\frac{\Delta t}{2}\right)}{\left(\frac{\Delta}{2}\right)^2} = 2\pi t \delta(\Delta). \quad (71)$$

Hence, the heat transfer rate can be derived from  $\langle b^\dagger b \rangle$  or Fermi's golden rule when first cutting off the heat baths first. The resulting rate is only valid in the long-time limit for  $t \gg \Delta^{-1}$  and for small coupling strength, since it is based on perturbation theory. The effect of the coupling to the heat baths is taken into account by averaging the rate  $R_{\text{FGR}}$  over the linewidth profiles. For two nanoparticles with  $\omega_a = \omega_b = \omega_{\text{sp}}$  having a finite linewidth  $\kappa_1$  and  $\kappa_2$  the long-time limit condition then translates into  $t \gg \kappa_1^{-1}, \kappa_2^{-1}$ .

## V. HEAT EXCHANGE BETWEEN TWO NANOPARTICLES - DETERMINATION OF THE PARAMETER $g$ IN THE MICROSCOPIC INTERACTION HAMILTONIAN $H_I$

Up to here we have discussed our model itself in some detail. To relate it to the heat transfer dynamics for the resonant radiative heat exchange between two nanoparticles, we still need to determine the coupling  $g$  for describing the heat transfer rate. To do this, we consider the heat flux between two nano-particles in the steady-state and determine  $g$  from that by comparing the heat transfer rate with the steady-state solution of our model.

### A. Heat transfer rate in steady state

The heat transfer rate between two nano-particles in steady state was derived for example in Refs. [10, 11, 17]. Its derivation is usually based on the fluctuation-dissipation theorem of the second kind [4, 5] which serves as the basis of Rytov's fluctuational electrodynamics [3]. Within this framework the power  $P$  transferred between two identical nanoparticles with temperatures  $T_1 > 0$  and  $T_2 = 0$  is [11]

$$P = \int_0^\infty \frac{d\omega}{4\pi^3} \hbar \omega \bar{n}_1 \text{Im}(\alpha)^2 \frac{\omega^6}{c^6} \left[ \frac{3}{\left(\frac{\omega}{c}d\right)^6} + \frac{1}{\left(\frac{\omega}{c}d\right)^4} + \frac{1}{\left(\frac{\omega}{c}d\right)^2} \right]. \quad (72)$$

This expression is only valid for particles with a radius  $r_0$  smaller than the dominant thermal wavelength and an interparticle distance  $d$  larger than their radii. Furthermore, multiple-

interactions are neglected as well as the contribution due to eddy currents.

Now, since we are interested in the power transferred by the resonant interaction of the localized surface modes of the nanoparticles we expect that the main contribution comes from the resonance of the polarizability  $\alpha$  at frequency  $\omega_{\text{sp}}$  which allows for approximating the above expression by

$$P \approx \hbar\omega_{\text{sp}}\bar{n}_1 F(\omega_{\text{sp}}) \int_0^\infty \frac{d\omega}{4\pi^3} \text{Im}(\alpha)^2 \quad (73)$$

introducing the function

$$F(\omega) = \frac{\omega^6}{c^6} \left[ \frac{3}{\left(\frac{\omega}{c}d\right)^6} + \frac{1}{\left(\frac{\omega}{c}d\right)^4} + \frac{1}{\left(\frac{\omega}{c}d\right)^2} \right]. \quad (74)$$

Therefore the heat transfer rate in steady state is

$$\begin{aligned} R_{\text{st-st}} &= \bar{n}_1 F(\omega_{\text{sp}}) \int_0^\infty \frac{d\omega}{4\pi^3} \text{Im}(\alpha)^2 \\ &= \bar{n}_1 F(\omega_{\text{sp}}) (4\pi r_0^3)^2 \frac{1}{2} \int_{-\infty}^{+\infty} \frac{d\omega}{4\pi^3} \left( \frac{3\text{Im}(\epsilon)}{|\epsilon + 2|^2} \right)^2. \end{aligned} \quad (75)$$

To further proceed we assume that we have metallic nanoparticles which can be described by the Drude model in Eq. (3). Inserting this expression in the integrand of  $R_{\text{st-st}}$  we obtain

$$R_{\text{st-st}} = \bar{n}_1 F(\omega_{\text{sp}}) (4\pi r_0^3)^2 \frac{\omega_{\text{sp}}^6 \Gamma^2}{2\pi^3} \left( \frac{3}{\epsilon_\infty + 2} \right)^2 \int_{-\infty}^{+\infty} d\omega \frac{1}{(\omega^2 - \omega_{\text{sp}}^2 + 2i\omega\Gamma)^2 (\omega^2 - \omega_{\text{sp}}^2 - 2i\omega\Gamma)^2} \quad (76)$$

introducing the surface mode frequency  $\omega_{\text{sp}} = \omega_p / \sqrt{\epsilon_\infty + 2}$  and its damping  $\Gamma = \gamma/2$ . The frequency integrand has four second-order poles in the complex frequency plane. We compute the integral by taking the two poles in the upper half plane into account and obtain assuming that  $\omega_{\text{sp}} \gg \Gamma$

$$R_{\text{st-st}} = \bar{n}_1 \frac{\omega_{\text{sp}}^2}{\Gamma} \frac{r_0^6}{2} F(\omega_{\text{sp}}) \left( \frac{3}{\epsilon_\infty + 2} \right)^2. \quad (77)$$

## B. Comparison with master equation approach

Since we have the steady-state result for the heat transfer rate between two identical nanoparticles in Eq. (77) we can determine the coupling constant  $g$  by comparing it to the steady-state solution of our model. Since expression (72) does not include multiple interactions between the nanoparticles it is in fact a first order perturbation result in  $\alpha^2$ .

Therefore, we compare it with the perturbation expression for the steady-state solution in Eq. (64) setting  $\kappa_1 = \kappa_2 = \Gamma$

$$R = \frac{g^2}{\Gamma} \bar{n}_1. \quad (78)$$

By comparison to  $R_{\text{st-st}}$  we can identify

$$g = \omega_{\text{sp}} \frac{r_0^3}{\sqrt{2}} \sqrt{F(\omega_{\text{sp}})} \frac{3}{\epsilon_{\infty} + 2}. \quad (79)$$

Since to leading order for small distances  $F(\omega_{\text{sp}}) \propto 1/d^6$  we have  $g \propto 1/d^3$  which is typical for a dipole-dipole interaction.

### C. Heat transfer dynamics for two nanoparticles

Finally, we have all the ingredients to determine the dynamics of the heat transfer rate for two nanoparticles supporting surface modes. When assuming that we have two gold nanoparticles then  $\omega_p = 1.4 \times 10^{16} \text{ rad/s}$ ,  $\epsilon_{\infty} = 3.7$  and  $\gamma = 2.79 \times 10^{13} \text{ s}^{-1}$  (see Fig. 2.1 on p. 25 of Ref. [27] for a fit to the Christy-Johnson data from Ref. [26]). It follows that the surface mode resonance frequency is  $\omega_{\text{sp}} = 5.86 \times 10^{15} \text{ rad/s}$  with the linewidth  $\Gamma = 1.4 \times 10^{13} \text{ s}^{-1}$ . If we consider a nanoparticle radius of  $r_0 = 20 \text{ nm}$  and an interparticle distance of  $d = 800 \text{ nm}$ , and  $d = 1200 \text{ nm}$  we find the heat transfer rate  $R/\Gamma$  plotted in Fig. 5. For times larger than  $1/\Gamma$  the heat transfer rate coincides with its steady-state expression. On the other hand, in the transient regime one can observe the dynamics of the heat transfer rate for times smaller than  $1/\Gamma \approx 72 \text{ fs}$ . As can be seen, for the considered distances we are mainly in the weak-coupling regime for which we have derived the coupling constant from the known steady-state heat flux expression. For distances smaller than  $d = 800 \text{ nm}$  the coupling becomes stronger. Finally, in the strong coupling regime the energy transfer rate is not a meaningful quantity so that we consider for this regime  $\langle b^\dagger b \rangle / \bar{n}_1$  rather than  $R/\Gamma$ . In Fig. 6 we plot  $\langle b^\dagger b \rangle / \bar{n}_1$  for  $d = 100 \text{ nm}$  which corresponds to  $g/\Gamma = 5.8$  showing clearly the Rabi oscillations.

## VI. CONCLUSION

We have introduced a model of two coupled dipoles which are both coupled to their own heat baths of independent oscillators. This model allows us to describe the heat transfer

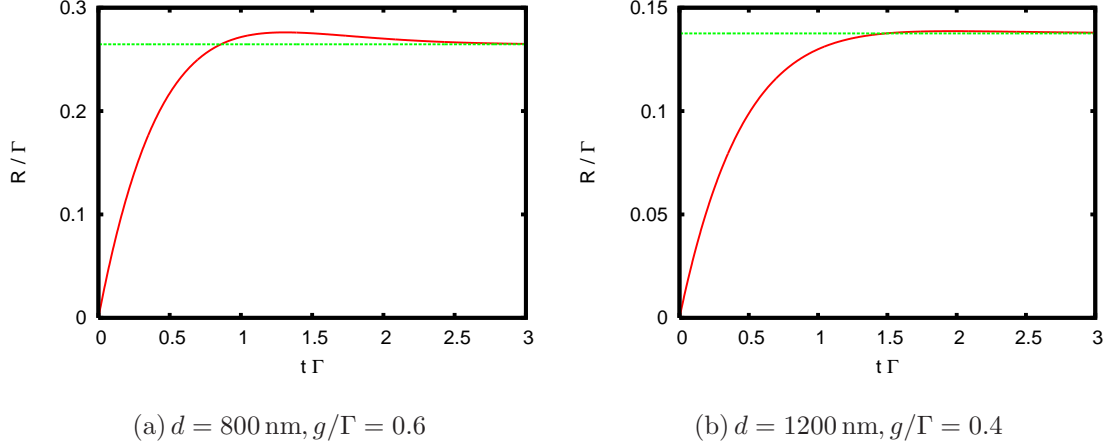


Figure 5: Heat transfer rate  $R/\Gamma$  from Eq. (62) between two nanoparticles normalized to the linewidth  $\Gamma$  of the nanoparticles surface mode resonances over time in units of  $\Gamma^{-1}$ . We use the coupling constant  $g$  from Eq. (79) with  $r_0 = 20 \text{ nm}$  and  $d = 800 \text{ nm}$  and  $d = 1200 \text{ nm}$ . The horizontal line is the steady-state expression from Eq. (63).

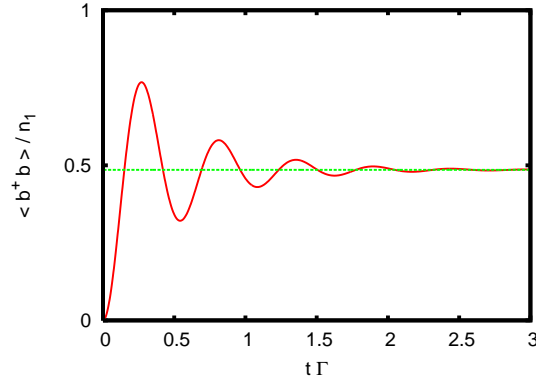


Figure 6: Mean occupation number  $\langle b^\dagger b \rangle / \bar{n}_1$  of the surface mode of nanoparticle  $B$  from Eq. (38) over time in units of  $\Gamma^{-1}$ . We use the coupling constant  $g$  from Eq. (79) with  $r_0 = 20 \text{ nm}$  and  $d = 100 \text{ nm}$ , hence  $g/\Gamma = 5.8$ . The horizontal line is the steady-state expression from Eq. (44).

dynamics between two nano systems. In particular, we have used this model to determine the heat transfer rate between two spherical nanoparticles which is due to the resonant interaction of the localized surface modes. Within our model we have derived the expression in the limit of short times as well as in the steady state regime and made a connection to the usual heat transfer calculations which are based on the fluctuation-dissipation theorem considering the steady-state regime only. We have shown that for small coupling strength between the nanoparticles the steady-state heat transfer rate can also be determined by

Fermi's golden rule when taking into account the finite widths of the resonant surface modes. Finally, we have studied the dynamical heat transfer rate for two gold nanoparticles in the transient regime for times shorter than the relaxation time of the surface modes and predict Rabi oscillations for the mean occupation number of the surface plasmons [1].

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